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(54) Crosslinkable oligomers.

(57) Multidimensional oligomers of the present invention are surprisingly useful for advanced composites because each generally has a use temperature greatly in excess of its curing temperature. The oligomers have essentially no arms, and comprise crosslinking phenylimide end caps condensed directly onto an aromatic hub (preferably, phenyl) through "commodity" polymeric linkages, such as amide, diimide, ether, or ester. For example, p-nadicimidobenzoylchloride can be condensed with triaminobenzene to yield a multidimensional, crosslinking amide oligomer. Short chains of ether/carbonyl aromatic chains can be included, if desired. Methods for making these high-performance oligomers with ether/carbonyl aromatic chains use an Uhlman ether synthesis followed by a Friedel-Crafts reaction.

EP 0 277 476 A2

MULTIDIMENSIONAL, CROSSLINKABLE OLIGOMERS

TECHNICAL FIELD AND BACKGROUND OF THE INVENTION

The present invention relates to multidimensional oligomers that include a hub and a plurality of radiating arms, each arm terminating at the periphery in a crosslinking end cap moiety. Such compounds have relatively low molecular weight, but cure to high performance composites useful at high temperatures.

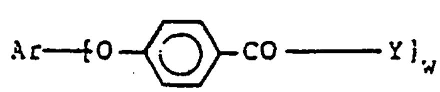
Epoxies dominate the composite industry today primarily because they are relatively low-cost and are easy to use. Epoxies, however, have low thermal stabilities and tend to be brittle. There is a need for high performance, temperature-resistant composites made by curing inexpensive, "commodity" starting materials that will be useful in conditions where epoxies cannot be used.

SUMMARY OF THE INVENTION

Composites possessing glass transition temperature greatly in excess of their curing temperatures can be prepared from multidimensional oligomers formed by the condensation of "commodity" starting materials.

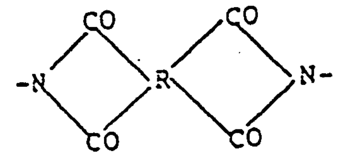
According to one aspect of the invention, there is provided a crosslinkable oligomer having a multidimensional morphology, the oligomer comprising a compound selected from the group consisting of:

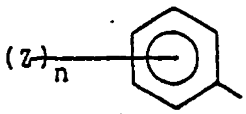
$$Ar \text{---} [P\text{-}Y]_w ;$$



; or

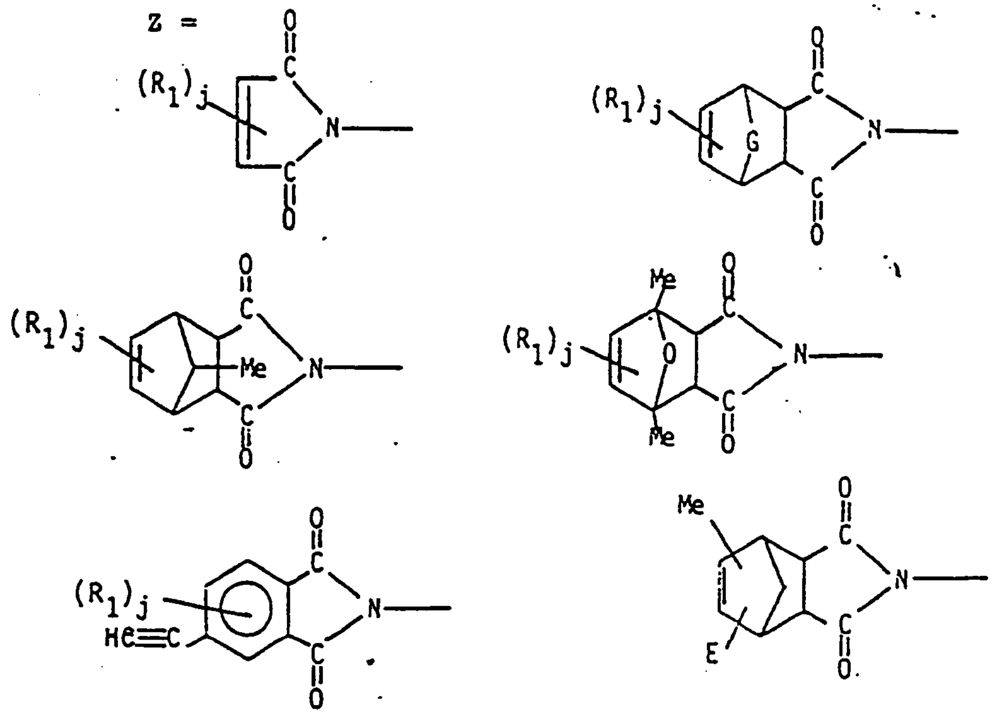
wherein w = an integer greater than 2 and not greater than the available number of substitutable hydrogens on the Ar group;
Ar = an aromatic moiety;
P = amide, ether, ester, or


;

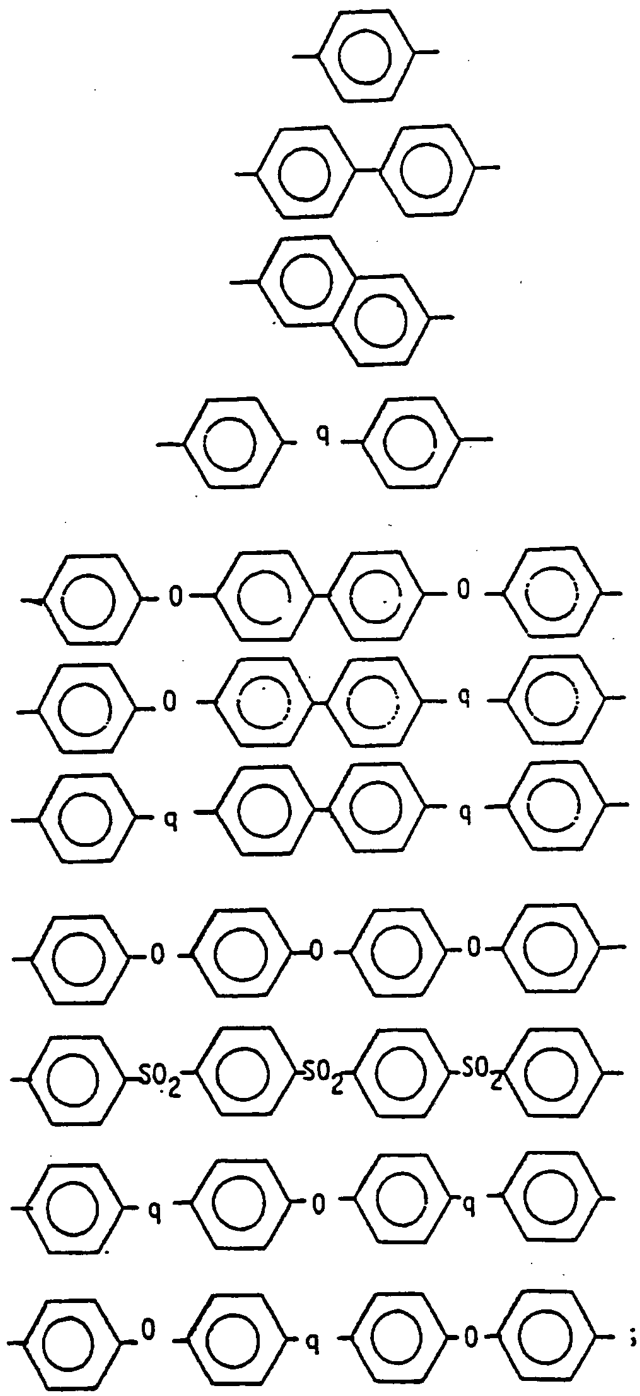
$Y = (Z)_n$  ;

$n = 1$ or 2;

$Z =$



R = an organic radical having a valency of four;
R_1 = any of lower alkyl, lower alkoxy, aryl, phenyl, or substituted aryl (including hydroxyl or halo-substituents);
j = 0, 1, or 2;
E = allyl or methallyl;
G = $-CH_2-$, -S-, -O-, or $-SO_2-$;
Q = an organic radical of valence two, and preferably a compound selected from the group consisting of:



q = $-SO_2-$, -CO-, -S-, or $-(CF_3)_2C-$, and preferably $-SO_2-$or -CO-.

As will be explained, these oligomers are prepared by the condensation of an aromatic hub and a suitable end cap moiety with or without a chain-extending group (Q) to provide short-armed, multidimensional oligomers of high thermal stability.

DETAILED DESCRIPTION OF THE INVENTION

Multidimensional morphologies in crosslinking oligomers produce composites having solvent resistance, high glass transition temperatures, and toughness upon curing. The resins and prepegs are readily processed prior to curing. The cured composites have glass transition temperatures (melt temperatures in excess of their curing temperatures). Such compounds can be readily made from "commodity" starting materials that are readily available at relatively low cost. The composites are cost competitive with epoxies, but possess better physical properties for aerospace applications (especially higher use temperatures).

Particularly preferred oligomers of the present invention have the general formula:

$$Ar-\left[P-Y\right]_w$$

wherein

Ar = an aromatic radial;

Y = a crosslinking end cap;

w = an integer greater than 2 and not greater than the available number of substitutable hydrogens on the Ar group;

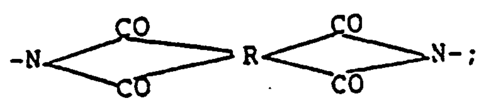
P = -CONH-,

-NHCO-,

-O-,

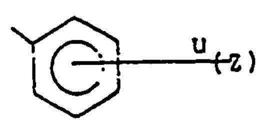
$-\overset{O}{\overset{\|}{C}}-O-$,

$-O-\overset{O}{\overset{\|}{C}}-$, or



; and

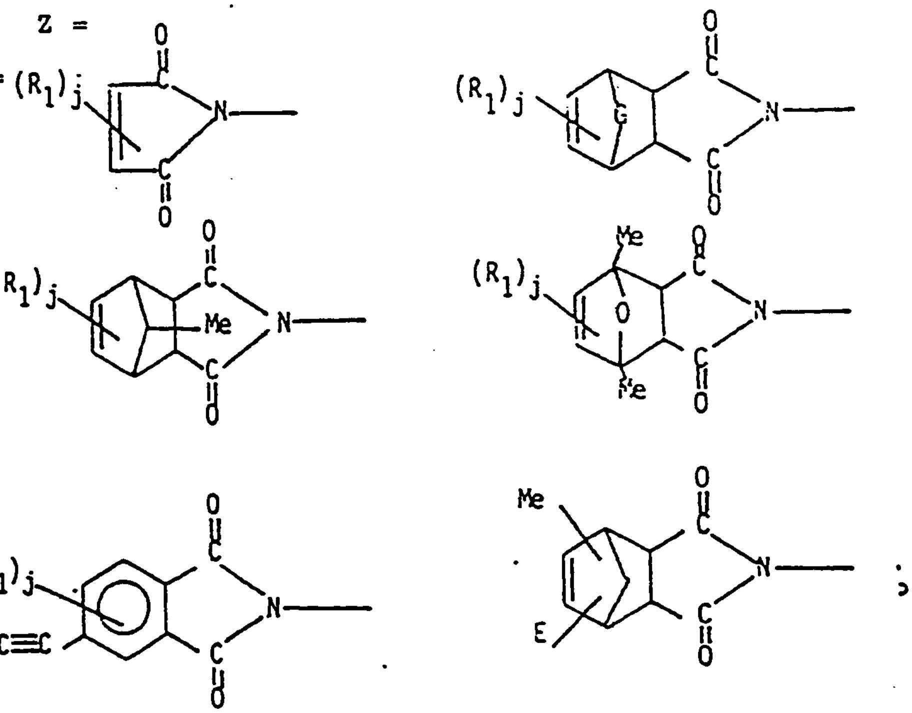
The crosslinking end cap (Y) is preferably a phenylimide having the formula:



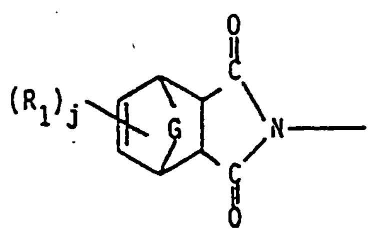
wherein n = 1 or 2

Z =

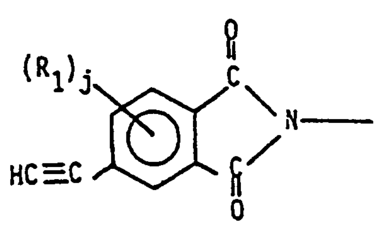
Z =



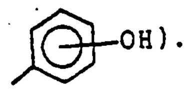
R_1 = any of lower alkyl, lower alkoxy, aryl, or substituted aryl (including hydroxyl or halo-on any replaceable hydrogen);
j = 0, l, or 2; and
G = $-CH_2-$, -S-, -S-, -O-, or $-SO_2-$.
The most preferred end caps include:



or



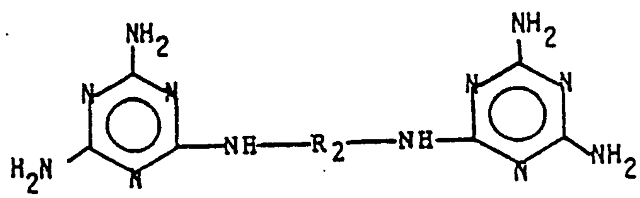
wherein
n = 1 or 2 (preferably 2);
j = 0, 1, or 2 (preferably 1);
G and R_1 are as previously defined (with R_1 preferably being



These multidimensional oligomers are made by the condensation of aromatic hub monomers with the end cap reactants in an inert atmosphere. For example, the hub might be

and the end cap, a radical as illustrated above terminated with an acid halide to form an amide linkage (NHCO) between the hub and the end cap. Alternatively, the hub might include the acid halide and the end cap the amine so that the condensation will yield an amide of opposite orientation (CONH). Ester or ether multidimensional oligomers of this general type are made in accordance with Examples I through VII of our copending application U.S.S.N. 810,817 by reacting an acid halide and a phenol. Diimide linkages are formed by reacting an amine-terminated hub with a dianhydride and an amine-terminated end cap.

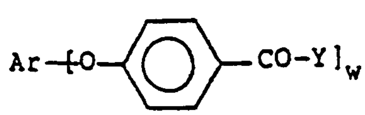
The hub (Ar) precursor preferably is selected from the group consisting of phenyl, naphthyl, biphenyl, azalinyl (including melamine radicals) amines or acid halides, or triazine derivatives described in U.S. Patent 4,574,154 (incorporated by reference) to Okamoto of the general formula:



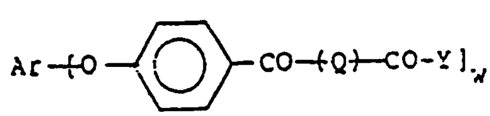
wherein R_2 is a divalent hydrocarbon residue containing 1-12 carbon atoms (and, preferably, ethylene).

Substantially stoichiometric amounts of the reactants are usually mixed together in a suitable solvent under an inert atmosphere to achieve the condensation. The reaction mixture may be heated, as necessary, to complete the reaction. Any of the oligomers can be used to form prepregs by application of the oligomers in a suitable solvent to suitable prepregging materials, and the prepregs can be cured in conventional vacuum bagging techniques at elevated temperatures to produce composites that have use temperatures in excess of their cure temperatures. the crosslinking end caps apparently bind the composites into a complex, 3-dimensional network upon curing by chemical induction or heating to yield a product having high thermal stability than the core temperature.

Compounds of the formula:

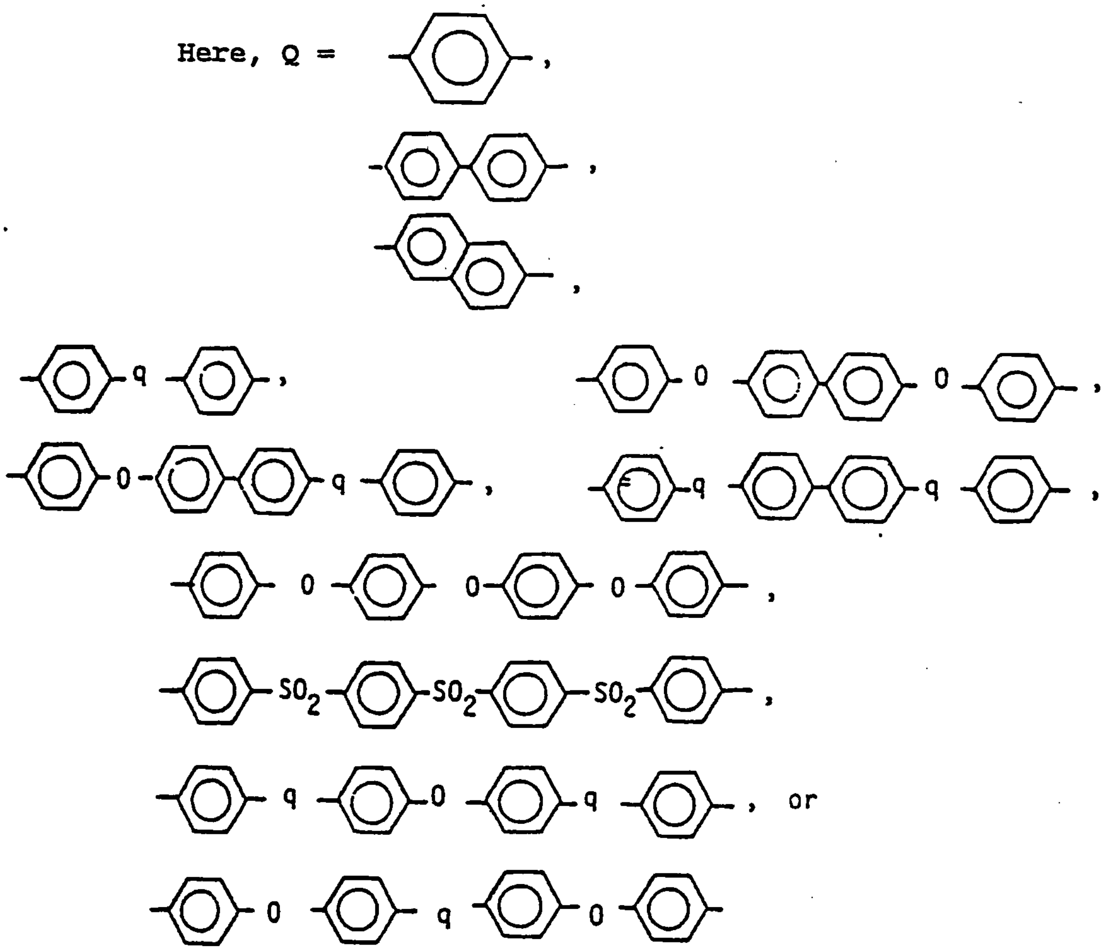


or



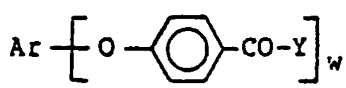
can also be synthesized with an Uhlman ether synthesis followed by a Friedel-Crafts reaction, as will be further explained.

Here, Q =

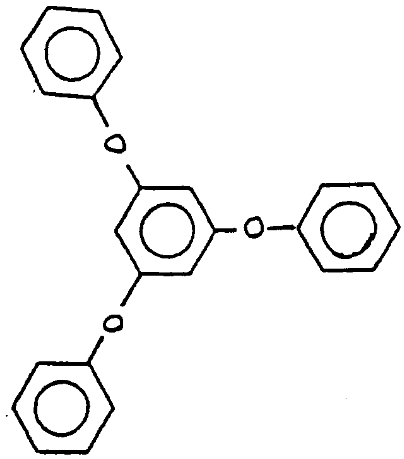


wherein q = $-SO_2$, -CO-, -S-, or $-(CF_3)_2-$, and preferably $-SO_2-$or -CO-.

To form the

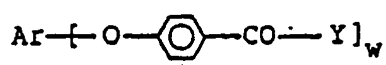


compounds, preferably a halo-substituted hub is reacted with phenol in DMAC with a base (NaOH) over a Cu Uhlman catalyst to produce an ether "star" with active hydrogens para-to the ether linkages. End caps terminated with acid halide functionalities can react with these active aryl groups in a Friedel-Crafts reaction to yield the desired product. For example, 1 mole of trichlorobenzene can be reacted with about 3 moles of phenol in the Uhlman ether reaction to yield an intermediate of the general formula:

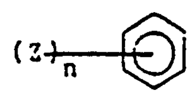


This intermediate can, then, be reacted with about 3 moles of (Y) - COCl to produce the final, crosslinkable, ether/carbonyl oligomer.

Similarly, to form the Ar [O - CO-Q-CO-Y]w compounds, the hub is extended preferably by reacting a halo-substituted hub with phenol in the Uhlman ether synthesis to yield the ether intermediate of the



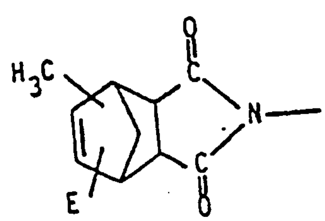
compounds. This intermediate is mixed with the appropriate stoichiometric amounts of a diacid halide of the formula XOX - Q - COX and an end cap of the formula



in the Friedel-Crafts reaction to yield the desired, chain-extended ether/carbonyl star and star-burst oligomers.

The end caps (Z) crosslink at different temperatures (i.e. their unsaturation is activated at different curing temperatures), so the cap should be selected to provide cured composites of the desire thermal stability. That is, the backbone of the oligomer should stable to at least the cure temperature of the caps. The multidimensional morphology allows the oligomers to be cured at a temperature far below the use temperature of the resulting composite, so completely aromatic backbones connected by heteroatoms are preferred to enhance the thermal stability.

United States Patent 4,604,437 is incorporated by reference. That patent describes a polymer made from substituted, unsaturated, bicyclic imides having end caps of the formula:

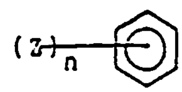


wherein
E = allyl or methallyl, and
n = 1 or 2.

These bicyclic imide nd caps are prepared from th analogous anhydride by condensation with an amine, and provide oligomers that cure in a temperature range between DONA (dimethyl oxynadic) and nadic caps.

While essentially any dianhydride (aliphatic or aromatic) can be used to form the diimide oligomers of the present inventi n, aromatic dianhydrides, such as pyromellitic dianhydride or benzophenonetetracarboxylic dianhydride, are preferred for cost, convenience, and thermal stability in the cured composite. If an aliphatic dianhydride is used, preferably the dianhydride is 5-(2,4-diketotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride (MCTC).

End caps of the formula



are

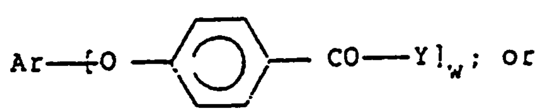
prepared by reacting an amine-substituted benzene, such as benzamine, with an anhydride in the manner outlined in U.S. Patent 4,604,437. One process for making the precursor anhydrides is described in U.S. Patent 3,105,839.

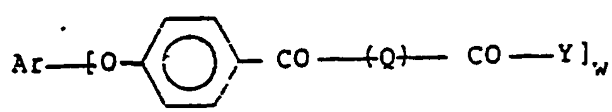
While preferred embodiments have been shown and described, those of ordinary skill in the art will recognize variation, modifications, or alterations that might be made to the embodiments that are described without departing from the inventive concept. Accordingly, the description should be interpreted liberally, and the claims should not be limited to the described embodiments, unless such limitation is necessary to avoid the pertinent prior art.

Claims

1. A crosslinkable oligomer having a multidimensional morphology, comprising a compound selected from the group consisting of:

$$Ar \text{—} [P\text{-}Y]_w ;$$



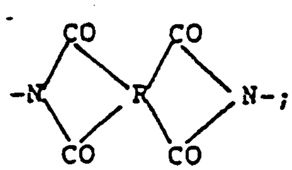


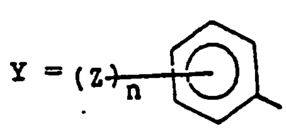
wherein

w = an integer greater than 2 and not greater than the available number of substitutable hydrogens on the Ar group;

Ar = an aromatic moiety;

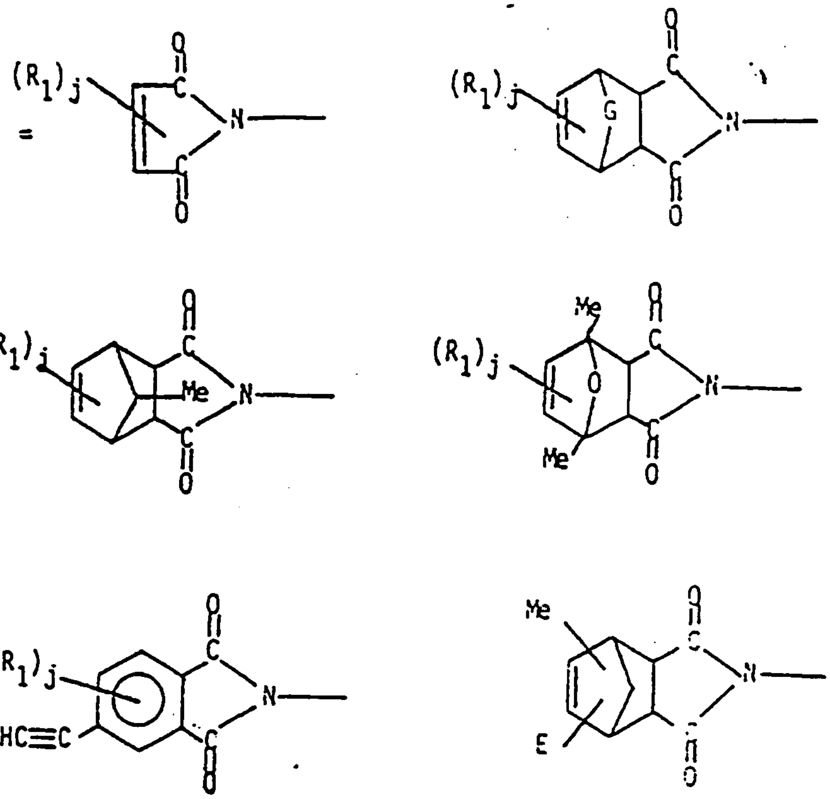
P = amide, ether, ester, or



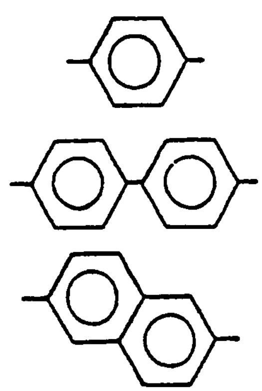


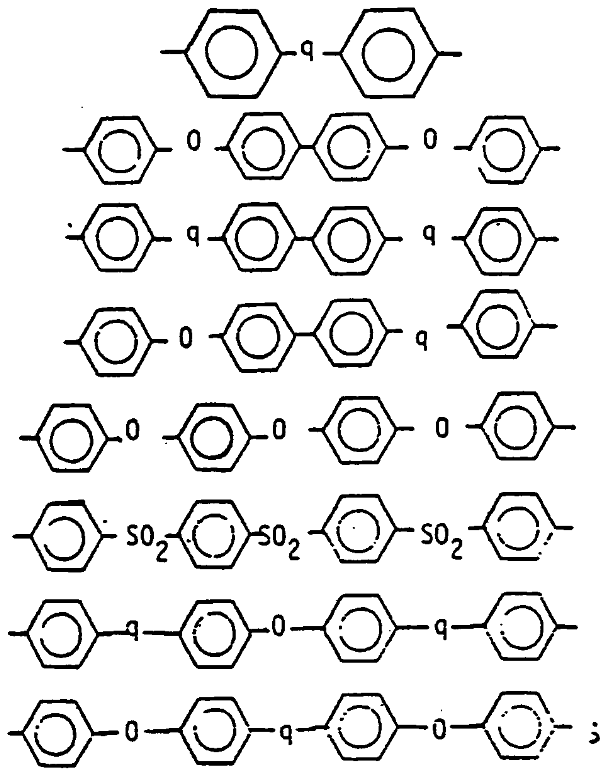
n = 1 or 2;
R = an organic radical having a valency of four;

Z =



R_1 = any of lower alkyl, lower alkoxy, aryl, phenyl, or substituted aryl;
j = 0, 1 or 2;
G = $-CH_2-$, -S-, -O-, or $-SO_2-$;
E = allyl or methallyl;
Q = a radical selected from the group consisting of:





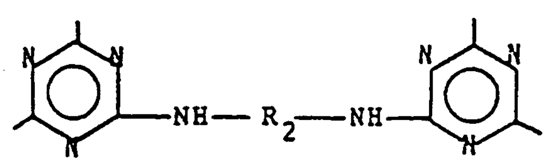
q = $-SO_2-$, $-CO-$, $-S-$, or $-(CF_3)_2C-$.

2. The oligomer of claim wherein the compound is selected from the group consisting of:

$Ar \text{—}[P\text{—}Y]_w$

3. The oligomer of claim 1 wherein Ar is selected from the group consisting of phenyl, biphenyl, azalinyl, naphthyl, or a triazine derivative of the formula: wherein R_2 = a divalent hydrocarbon residue containing 1-12 carbon atoms, and wherein, if Ar is a triazine derivative, P = -NHCO-.

4. The oligomer of claim 2 wherein Ar is selected from the group consisting of phenyl, biphenyl, azalinyl, naphthyl, or a triazine derivative of the formula:



wherein R_2 = divalent hydrocarbon residue containing 1-12 carbon atoms, and wherein, if Ar is a triazine derivative, then P = -NHCO-.

5. The oligomer of claim 1 wherein Ar is selected from the group consisting of phenyl, biphenyl, naphthyl, or azalinyl.

6. The oligomer of claim 1 wherein Ar is phenyl and w = 3 or 4.

7. A prepreg comprising a suitable fiber cloth and an effective amount of the oligomer of claim 1.

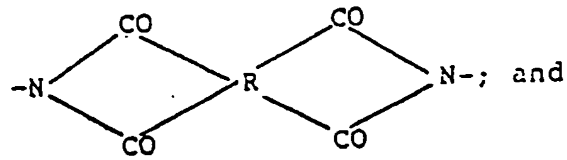
8. A composite comprising a cured oligomer of claim 1.

9. A composite comprising the cured prepreg of claim 7.

10. The oligomer of claim 2 wherein P is -NHCO-.

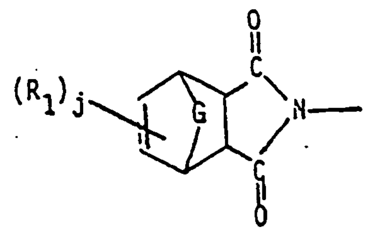
11. The oligomer of claim 2 wherein P is -CONH-.

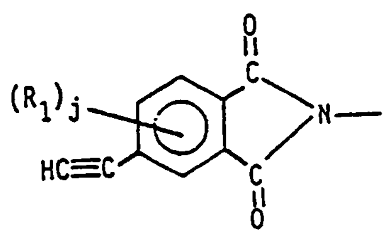
12. The oligomer of claim 2 wherein P is



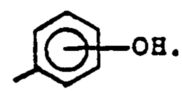
wherein R = a residue of pyromellitic dianhydride, benzophenonetetracarboxylic dianhydride, or 5-(2,4-diketotetrahydrofury)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride.

13. The oligomer of claim 2 wherein Y is selected from the group consisting of



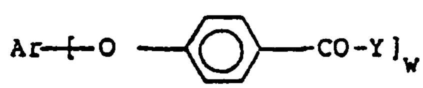


14. The oligomer of claim 13 wherein R_1 is



15. The oligomer of claim 1 wherein n = 2.

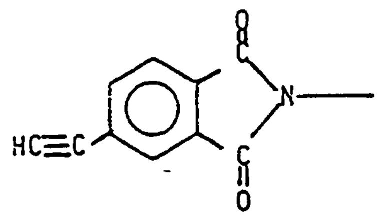
16. The oligomer of claim 1 wherein the compound is selected from the group consisting of:



17. The oligomer of claim 16 wherein Ar is selected from the group consisting of phenyl, biphenyl, naphthyl, or azalinyl.

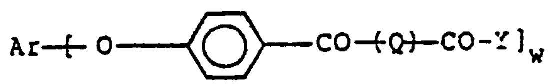
18. The oligomer of claim 16 wherein Ar is phenyl and w = 3 or 4.

19. The oligomer of claim 18 wherein Z is



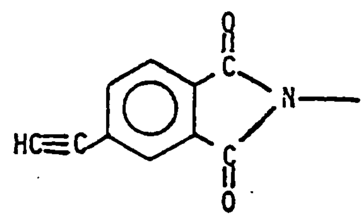
and w = 3.

20. The oligomer of claim 1 wherein the compound is selected from the group consisting of:



21. The oligomer of claim 20 wherein Ar is selected from the group consisting of phenyl, biphenyl, naphthyl, or azalinyl.

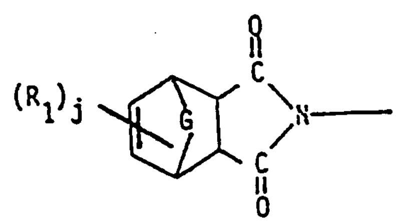
22. The oligomer of claim 21 wherein Z is:

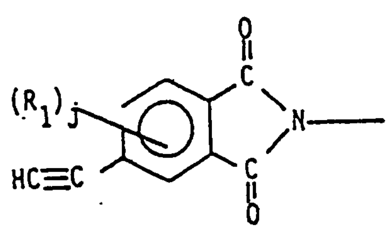


and w = 3.

23. The oligomer of claim 2 wherein Ar is phenyl and w = 3 or 4.

24. The oligomer of claim 23 wherein Z is selected from the group consisting of:



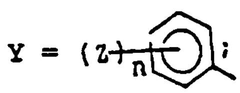


25. A method for making an oligomer of the general formula:

$Ar{+}NHCO{-}Y]_w$

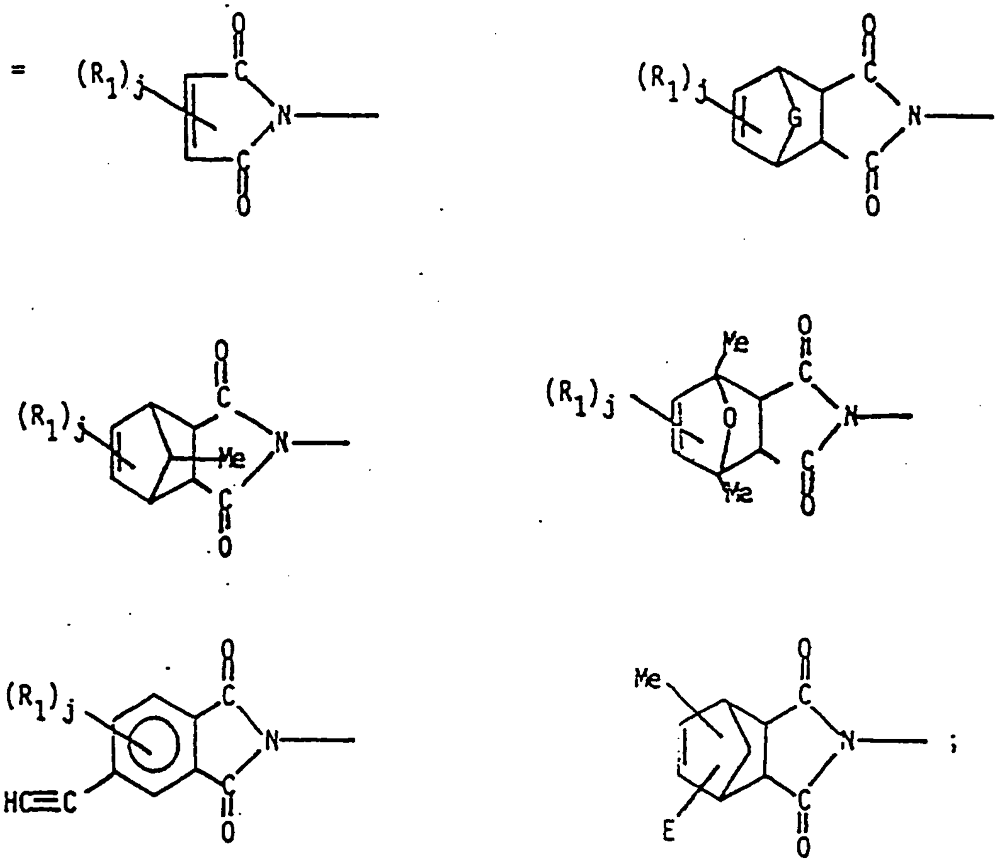
wherein

Ar = an aromatic moiety;
w = 3 or 4;



n = 1 or 2;

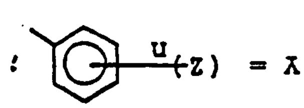
Z =



R_1 = any of lower alkyl,, lower alkoxy, aryl, phenyl, or substituted aryl;
j = 0, 1, or 2; and
G = $-CH_2-$, -S-, -O-, or $-SO_2-$,

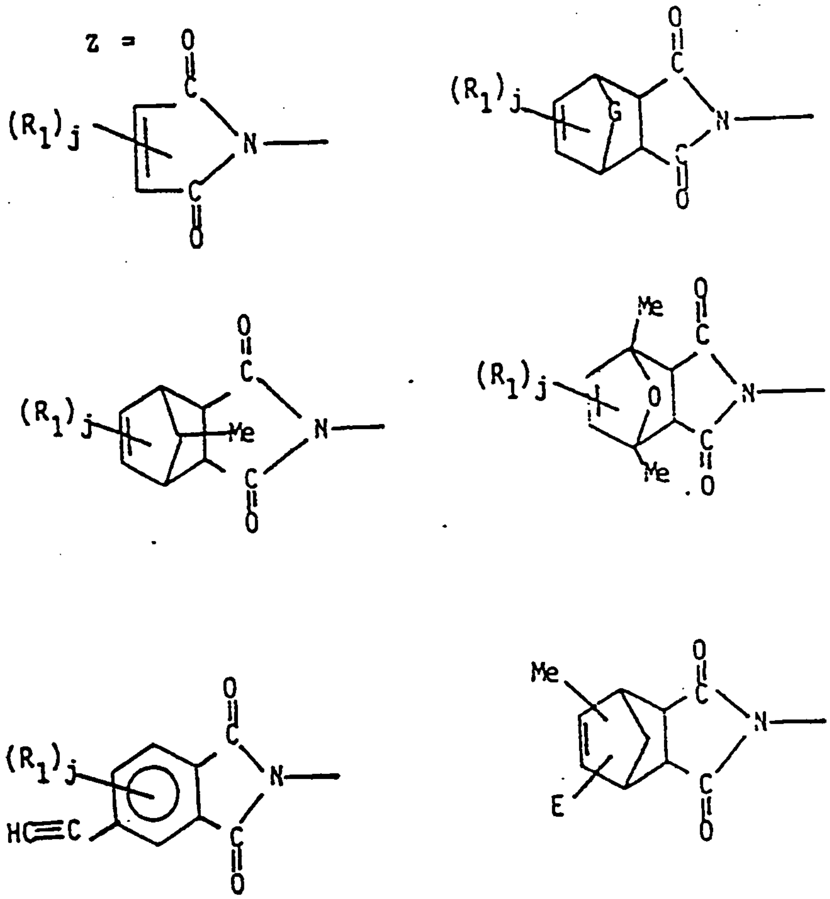
comprising the steps of reacting at lest one mole of $Ar-NH_2$ with at least w moles of Y-COX in a suitable solvent under an inert atmosphere.

26. A method for making an oligomer of the general formula:
$Ar \{ CONH\text{-}Y]_w$
wherein
Ar = an aromatic moiety; w = 3 or 4;



n = 1 or 2;

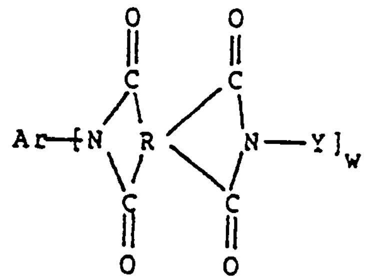
Z =



R_1 = any of lower alkyl, lower alkoxy, aryl, phenyl or substituted aryl;
j = 0, 1, or 2;
G = $-CH_2-$, -S-, -O-, or $-SO_2-$,

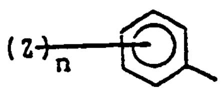
comprising the steps of reacting at least one mole of Ar-COX with at least w moles of $Y-NH_2$ in a suitable solvent under an inert atmosphere.

27. A method for making an oligomer of the general formula:

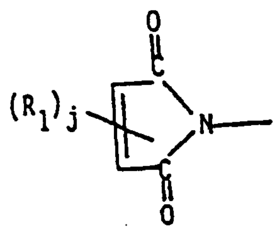


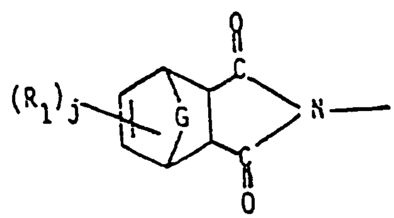
wherein Ar = an aromatic moiety;

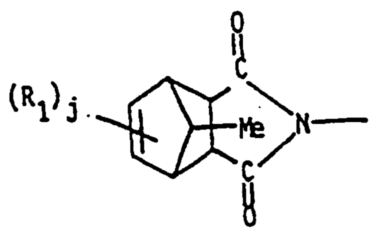
w = 3 or 4;

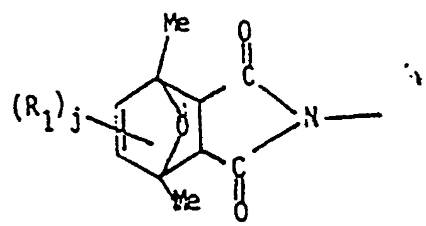
Y =  ;

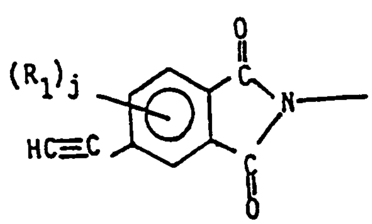
n = 1 or 2;

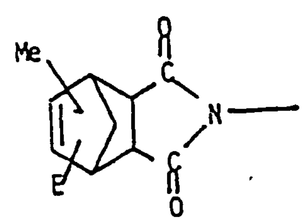
Z = 







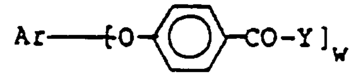




R = an organic radical having a valency of four;
R_1 = any of lower alkyl, lower alkoxy, aryl, phenyl, or substituted aryl;
j = 0, 1, or 2;
G = $-CH_2-$, -S-, -O-, or $-SO_2-$,

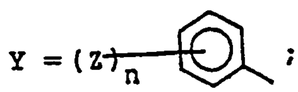
comprising the steps of reacting at least on mole of Ar $(NH_2)_w$ with at least w m l s of a dianhydride containing the R radical and with at least w moles of Y-NH_2 in a suitable solvent under an inert atmosphere.

28. A method for making an oligom r of the general formula:



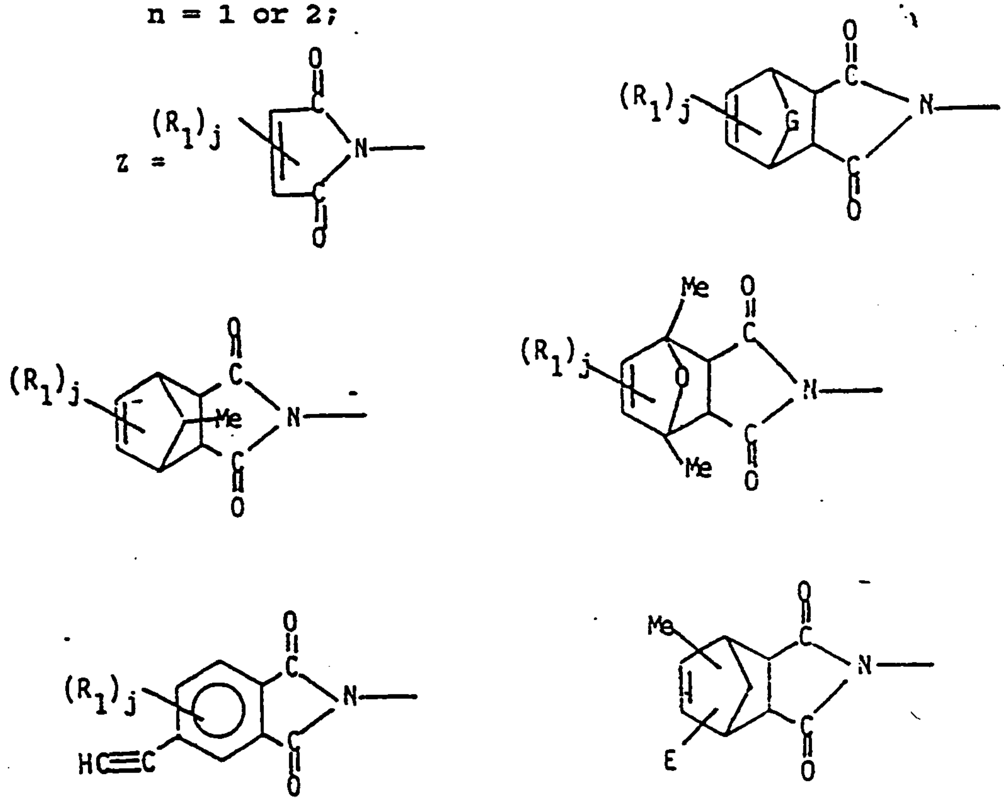
wherein
Ar = an aromatic moiety;
w = 3 or 4;

w = 3 or 4;



n = 1 or 2;

Z =



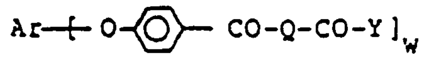
R_1 = any of lower alkyl, lower alkoxy, aryl, phenyl, or substituted aryl;
j = 0, 1, or 2;
G = $-CH_2-$, -S-, -O-, or $-SO_2-$,

comprising the steps of:

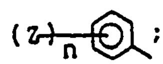
(a) reacting a halo-substituted Ar moiety with at least a stoichiometric amount of phenol in an Uhlman ether synthesis in DMAC in the presence of a base and an Uhlman copper catalyst to form an aryl ether intermediate; and

(b) reacting the aryl ether intermediate with at least a stoichiometric amount of Y-COX under Friedel-Crafts conditions in a suitable solvent to produce the oligomer.

29. A method for making an oligomer of the general formula:

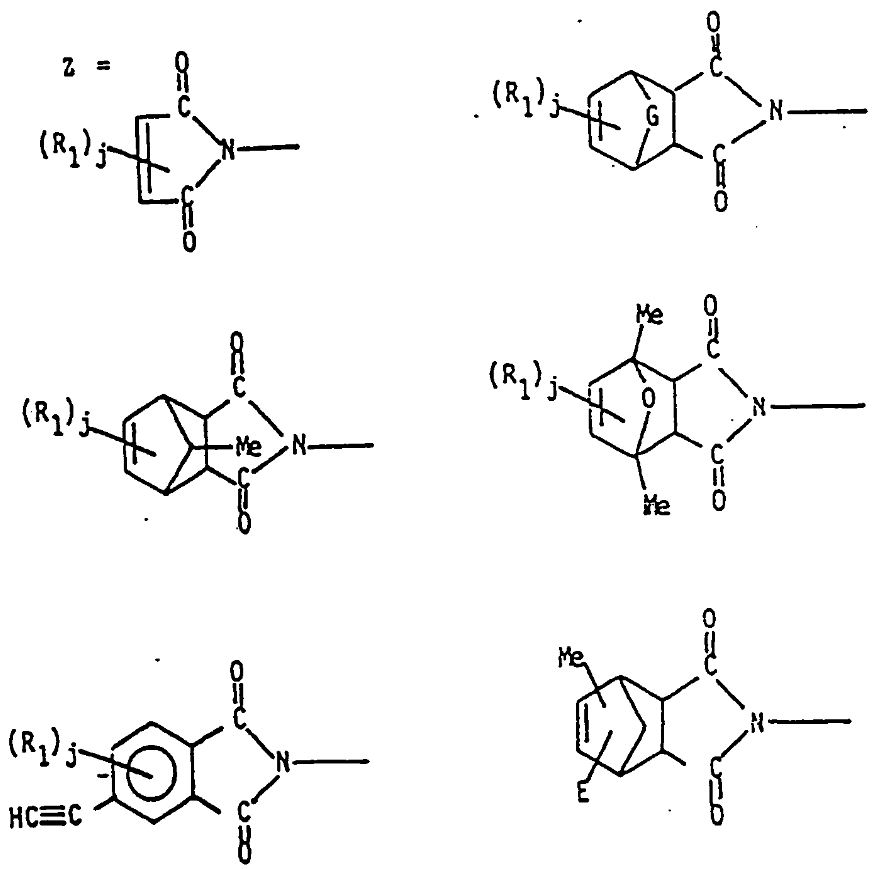


wherein
Ar = an aromatic moiety;
w = 3 or 4;

Y =  ;

n = 1 or 2;

Z =

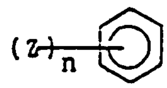


Q = an organic, divalent residue of a diacid halide;
R_1 = any of lower alkyl, lower alkoxy, aryl, phenyl, or substituted aryl;
j = 0, 1, or 2; and
G = $-CH_2-$, -S-, -O-, or $-SO_2$.

comprising the steps:

(a) reacting a halo-substituted Ar m iety with at l ast a stoichiometric amount of phenol in an Uhlman ther synthesis in DMAC in the presence of a base and an Uhlman copper catalyst to form an aryl ether intermediate; and

(b) reacting the aryl eth r intermediate with at least a stoichiometric amount of a diacid halide of the general formula XOC-Q-COX and with at least a stoichiometric amount of



under Friedel-Crafts conditions in a suitable solvent to produce the oligomer.

30. The product of the process of claim 28.

31. The product of the process of claim 29.